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UNPUBLISHED PRELIMINARY DATA

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FUNDAMENTAL ATOM CHEMISTRY WITH APPLICATIONS TO THE CHEMISTRY OF THE UPPER ATMOSPHERE

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Precise kinetic data for the conversion of 3:1 ortho-paratritium into 1:1 ortho-paratritium on a coconut charcoal at liquid neon temperature have been obtained. The publication of these data will appear in Zeitschift fur Naturforschung in March 1963. (Twenty-five copies of this manuscript were forwarded to NASA in November 1962).

The half-lifetime for the conversion at 27.4°K (liquid neon) was found to be one minute; back conversion on the same coconut charcoal at the temperature of liquid nitrogen (77.4°K) gave a half-life of 0.92 minutes. For hydrogen under identical conditions the half-lifetime was twenty-four times slower. To a first approximation the magnitude of the difference between hydrogen and tritium results in a factor of eight when one considers the transition probability expression derived by Wigner[1] for the homogeneous conversion in the gas phase. This marked variation between hydrogen and tritium is a most striking and interesting result and deserves further investigation. In this connection the effect of ions in the gaseous and solid state is now being studied.

Currently we are engaged in establishing the kinetics for the following: conversion of tritium in a solid lattice containing hydrogen; back conversion of paratritium (1:1) ortho-paratritium mixture in the presence of nitric oxide at room temperature, which is an independent measure of the nuclear magnetic moment; half-lifetime of conversion for pure tritium at the temperature of liquid helium; and the conversion of tritium on silica gel.

Preliminary results indicate a half-lifetime of 100 minutes for the mixture of hydrogen and tritium in the solid state. For the homogeneous back conversion of tritium in the presence of nitric oxide the measured half-lifetime was 17 minutes; this result agrees with the data reported by Farkas[2] for hydrogen back converting under similar conditions, allowance being made for the change of mass as required by the transition probability expression

of Wigner. Measurements related to the solid phase conversion and conversion on silica gel are in procedure.

At the Spring Meeting of the American Chemical Society in March 1963 a second paper on the tritium system will be presented and published in the Journal of the American Chemical Society. Prior to this time the requisite copies of this paper will be forwarded to NASA.

Future work will be directed toward establishing the effects of the ions produced by the radioactive decay of tritium on the mechanism of conversion for the homogeneous and heterogeneous phases. In the future after completing our experimentation on ortho- and paratritium we plan to conduct exploratory experiments on ortho- and para $N_{14} - N_{14}$ and $N_{15} - N_{15}$ and on the three methane systems. We hope that the knowledge acquired with the ortho- and paratritium experiments will help us to make a successful approach to this very tempting but experimentally difficult field.

Literature

Copies of papers discussed at the Informal Conference on Photochemistry in Brussels in June, 1962 are attached. This work was supported in part by this grant.

References

(1) E. Wigner, Z. f. physikal. Chemie, B, 19, 203 (1932).

(2) A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen", Cambridge Univ. Press, 1935.

Chemical Reactions of Excited Molecules*

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ABSTRACT

The excited molecules are produced by use of a surface catalyst. The chemical reactions of the nitrogen excited molecules ($N_2A^3\Sigma_u^+$) with different substances are discussed along with the reaction of the excited oxygen molecule ($O_2A^3\Sigma_u^+$) with oxygen and nitric oxide. The interaction of highly vibrationally excited OH radicals is also discussed.

* Discussed at the Informal Conference on Photochemistry at the University of Brussels, June 1962
Abstract will appear in the Bull. Soc. Chim. Belg, spring 1963

Chemiluminescent Reactions of Major Importance for the Upper Atmosphere*

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ABSTRACT

A huge reservoir of oxygen atoms (and to a minor extent nitrogen atoms) is present in the upper atmosphere, extending upward from about 100 kilometers. This abundance of atoms would be sufficient for substantial illumination of the night sky if appropriate reactions could be found. In the pressure region of 1 millimeter to an atmosphere, the 2-body collision reactions yielding light play a minor role. At pressures substantially below one millimeter, these reactions become dominant and may be the answer for this problem. A series of reactions, including nitrogen, sulfur and phosphorus compounds, the resulting light emission, and related problems are discussed.

*Delivered at the Informal Conference on Photochemistry at the University of Brussels, June 1962.
Paper and abstract will appear in the Bull. Soc. Chim. Belg., spring 1963.

CHEMILUMINESCENT REACTIONS OF MAJOR IMPORTANCE FOR THE UPPER ATMOSPHERE*

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The release of nitric oxide in the upper atmosphere six years ago by Dr. Zelikoff and his group[1] gave striking evidence for the existence of the chemosphere and particularly the relatively high concentration of oxygen atoms in this region. This paper discusses some considerations and laboratory experiments we have made concerning possible chemical releases and their effect on the upper atmosphere; and also what information might be obtained in this way about the nature of the upper atmosphere.

The solar radiation has an intensity which is a maximum in the visible region around 5000 A. In the upper atmosphere regions where the total pressure is one micron or less, one need consider only radiation which has a very high absorption coefficient. Radiation below 1800 A is absorbed by oxygen in this region to form O-atoms. Still lower wavelengths starting about at Lyman α (1216A) can make both ionization and dissociation precesses in the atmosphere. This sum of effective radiation is less that a per mil of the total energy of solar radiation.

This release of NO by Dr. Zelikoff and his group at about 106 km gave a luminosity which was almost exactly what was predicted. The nitric oxide reacts with O-atoms giving the well-known reaction:

$$NO + O \rightarrow NO_2 + h\nu; \quad k \approx 3.10^{-17} \qquad (1) \quad \text{(Ref 2)}$$

which may be followed by

$$NO_2 + O \rightarrow NO + O_2; \quad k \approx 10^{-12} \qquad (2)$$

The luminosity resulting from the NO release was readily observable indicating the presence of O-atoms. If the O-atoms had a concentration of $1 - 3 \times 10^{12}$ particles per cubic centimeter, than there would be one photon emitted per NO molecule by reaction (1) in every few hours. Actually, however, the glow disappeared in a fraction of an hour and at the time we speculated that this could be due to nitrogen atoms via:

$$N + NO \rightarrow N_2 + O : \quad k = 10^{-11} \qquad (3)$$

This idea that the N-atoms might be in sufficient concentration to interfere has not been widely accepted.

We have been looking for other chemicals to release which might give

1) more luminosity (per pound)
2) avoid destruction by N-atoms (or other loss mechanism)
3) indicate the N-atom concentration

When considering ways to have a more intense luminosity the question also arises as to what is the amount of energy stored as dissociation energy in the upper atmosphere and what is the number of light quanta which could be emitted in a process which emits one light quanta in the visible for each O-atom or for each pair of O-atoms. Assuming a maximum O-atom concentration in the 100 km altitude region of 10^{12} particles per cm^3, and a scale height of 10 km = 10^6, we see that, per cm^2, 10^{18} O-atoms are present during the night. By recombination, these 10^{18} O-atoms could release an energy equivalent of 0.1 cal/cm^2. Since the sun radiates about 10^{17} light quanta in the visible, the O-atoms stored in the upper atmosphere are sufficient, if an adequate chemical reaction could be found, to emit for a few seconds a light intensity equivalent to the luminosity of the sun during daytime. Obviously this high intensity - short duration emission is not practical to achieve. It is well in the realm of possibility, however, to release substantial amounts of a chemical with rockets in the regions where the O-atoms are most abundant and thereby induce photochemical reactions over wide areas. The emission may be sufficient to be easily seen from the ground, or even to brighten the night sky for several hours to a degree more than that of a full moon (more than 10^{12} light quanta per centimeter square per second).

I remember from over thirty years ago when we had been first studying reactions with oxygen atoms, that hydrogen sulfide gave a beautiful intense blue emission.[4] This glow is also readily observed with the reaction of O-atoms with sulfur, carbonyl sulfide, and carbon disulfide. A release of such a chemical might give a high intensity of light via:

$$SO + O \rightarrow SO_2 + h\nu \; ; \quad k = 3.10^{-16} \qquad (4)$$

For CS_2 we have studied the reaction and it probably follows a multi-step oxidation at these low pressures:

$$CS_2 + O \rightarrow CS + SO \; ; \quad k_5 \sim 10^{-12} \qquad (5)$$

$$CS + O \rightarrow CO + S \; ; \quad k_6 \sim 10^{-12} \qquad (6)$$

$$S + O_2 \rightarrow SO + O \; ; \quad k_7 \sim 10^{-12} \qquad (7)$$

$$SO + O \rightarrow SO_2 + h\nu \quad k_4 \sim 3.10^{-16} \qquad (4)$$

Reactions (5-7) appear to be fast with efficiencies of 10^{-3} or better while reaction (4) may be 10^{-6} or better. The coefficients indicated are estimated from preliminary work at room temperature from 100 microns down to 5 microns.

Reactions (5-7) consume rapidly O-atoms without light emission. Therefore a release of CS_2 in the upper atmosphere may yield a dark center with a bright blue shell which would grow with time. Unfortunately, there can be no regeneration of the SO via

$$SO_2 + O \rightarrow SO + O_2 \qquad (8)$$

It might be well at this point to compare the relative intensities of SO emission resulting from reaction (4) and NO emission from reaction (1). It is true that NO may be regenerated by reaction (2), while SO is not regenerated by reaction (8). The reaction rate of NO is, however, smaller ($k = 3.10^{-17}$) compared to that from SO ($k = 3.10^{-16}$). Furthermore the NO_2 produced by reaction (1) is apparently not available for regeneration because of reaction with N-atoms. Therefore, the release of a sulfur compound should give a substantially brighter luminosity.

Because of the possible interference of N-atoms in the nitric oxide release, we decided to investigate the mixed N-atom-O-atom reaction with sulfur compounds. We have tried the effect of N-atoms with a mixture of carbon disulfide and O-atoms and it not only doesn't interfere, it can actually enchance the total emission via the following reactions:*

$$CS_2 + O \rightarrow CS + SO \quad ; \quad k_5 \sim 10^{-12} \qquad (5)$$

$$CS + O \rightarrow CO + S \quad ; \quad k_6 \sim 10^{-12} \qquad (6)$$

$$S + O_2 \rightarrow SO + O \quad ; \quad k_7 \sim 10^{-12} \qquad (7)$$

$$SO + N \rightarrow S + NO \quad ; \quad k_{10} \sim 10^{-13} \qquad (9)$$

$$NO + O \rightarrow NO_2 + h\nu \quad k_1 \sim 3.10^{-17} \qquad (1)$$

$$SO + O \rightarrow SO_2 + h\nu \quad ; \quad k_8 \sim 3.10^{-16} \qquad (4)$$

The blue emission from (4) is not only enhanced by the production of O-atoms from N-atoms via Reactions (9) and (7), but also the color may change to yield a more whitish glow with time due to light emission by reaction (1). This effect was readily observed in the laboratory. Reaction (9) should be of basic importance for a sulphur or NO plus sulphur release in the upper atmosphere since the SO will have the effect to destroy the N-atoms and hence the resulting NO may have a substantial longer lifetime at least near the center of the release.

The role of N-atoms in the upper atmosphere is not entirely clear because of the lack of direct experimental evidence for the concentration and duration in the upper atmosphere. The N-atoms should have a lifetime of some hours at 100 kilometers (3) if they were consumed only by the reaction:

$$N + O_2 \rightarrow NO + O \quad ; \quad k_{11} = 10^{-16} \qquad (10)$$

Glows observed from the grenade releases may[5] be due to a shock wave which would accelerate reaction (10), with the subsequent reaction of NO with O-atoms in reaction (1).

*These reactions have been studied by Dondes and Liuti in detail. This work is being prepared for publication.

There arises the interesting problem of what other substances could be considered for such releases and what properties they should possess. Since the release of these substances will take place at very low pressures O-atom concentrations are highest, it would be preferred to have two-body reactions, since three-body reactions may be neglected. The two-body mechanism may be of two types:

$$AB + O \rightarrow AO^* + B$$
$$AO^* \rightarrow AO + h\nu \qquad \text{Type I}$$

and

$$X + O \rightarrow XO^*$$
$$XO^* \rightarrow XO + h\nu \qquad \text{Type II}$$

At present we don't know any reactions of Type I involving O-atoms which would emit light in the visible with a high efficiency. We are therefore limited to Type II. To this group belongs reaction (1), which can be written in the form as above as:

$$NO + O \rightarrow NO_2^*$$
$$NO_2^* \rightarrow NO_2 + h\nu$$

Other representatives of this type of substance which have to be considered are metals release directly, or as metal organic compounds, or as volatile inorganic compounds. Unfortunately these reactions are difficult to study and simulate in the laboratory, because usually metal oxides are formed which will deposit on the walls of the vessel and catalytically destroy the O-atoms. The ideal metal could behave in two ways:

(1) $M + O \rightarrow MO + h\nu$ (a)
$MO + O \rightarrow M + O_2$ (b)

(2) $MO + O \rightarrow + MO_2 + h\nu$ (a)
$MO_2 + O \rightarrow MO + O_2$ (b)

The light emission should be in the region where the eye is most sensitive and the MO or MO_2 should not undergo a chemical reaction with N-atoms which stops the chain. To properly investigate these types of reactions, we would need a very large reaction vessel, so that the wall effects would become reduced. We made all our experiments in a reaction vessel of 50 liters at about 10-20 micron pressure. This pressure is

about by a factor 100 lower than most experiments which are performed with atoms generated in a glow-discharge, but still a factor 10 higher than the pressure in the chemosphere. We would like to emphasize, that under our experimental conditions we came nearer to the condition which prevail in the chemosphere, than most of the experiments performed on these lines.

We investigated a series of the metal organic compounds (6). From these substances $Al(CH_3)_3$ gave, with O-atoms, a most beautiful white luminosity. In the figure can be seen the spectrum of light emitted. The dissociation energy of AlO is quoted as $D_o \sim 3.75$ volts in G. Herzberg, Spectra of Diatomic Molecules, 1951. This dissociation energy would be in line with the observed spectrum which extended to about 3800 A. A chain reaction (5) is therefore possible via:

$$Al + O \rightleftarrows AlO^* \rightarrow AlO + h\nu$$

and

$$AlO + O \rightarrow Al + O_2$$

This would fulfill both properties which one would desire for a chemical substance for release, namely a luminosity which is predominantly in the visible, and also a chain mechanism to regenerate the reactant.

At present we are designing an experimental arrangement which can extend the work still lower pressures to more nearly simulate the Chemosphere.

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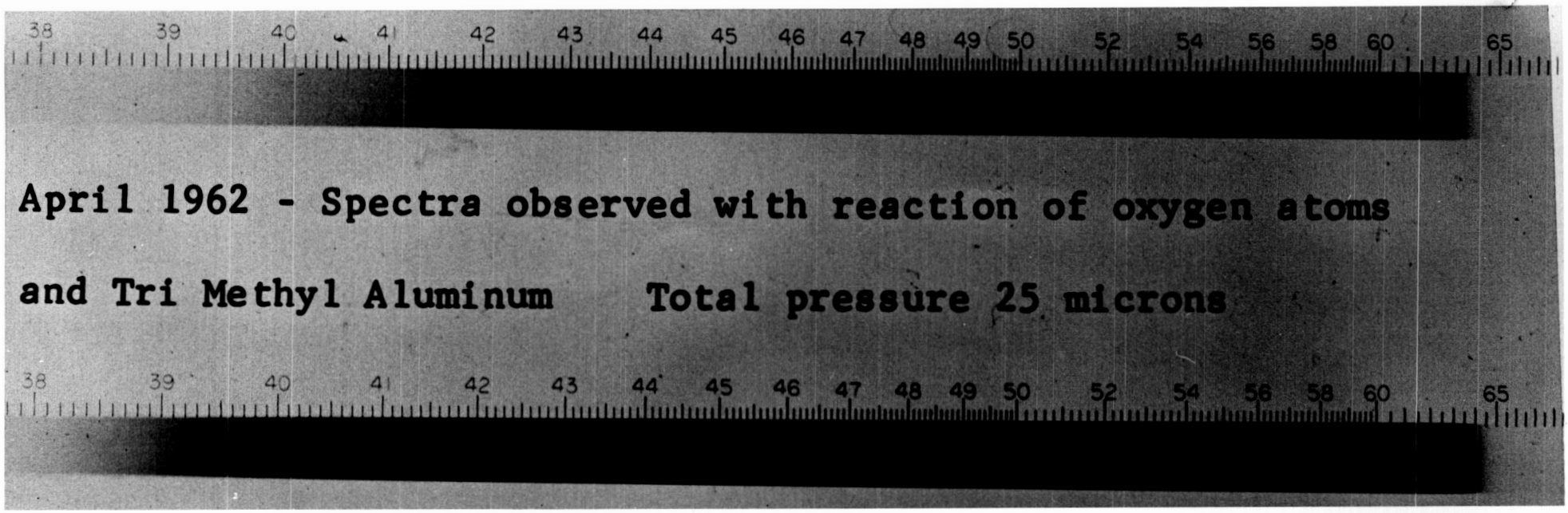
38 39 40 41 42 43 44 45 46 47 48 49 50 52 54 56 58 60 65
April 1962 - Spectra observed with reaction of oxygen atoms
and Tri Methyl Aluminum Total pressure 25 microns
38 39 40 41 42 43 44 45 46 47 48 49 50 52 54 56 58 60 65

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References:

1. Marmo, Pressman, Aschenbrand, Jursa, and Zelikoff; "The Threshold of Space", Pergamon Press, 1957, p. 235

2. A. Fontijn and H. I. Schiff; "Chemical Reactions in the Lower and Upper Atmosphere" Interscience Publishers (Wiley), 1961, p. 239. (Although there seems to be some doubt if the light emission is directly by this two-body reaction, we still favor this in preference to a three-body complex mechanism.)

3. The values for rate coefficient pertinent to many upper atmosphere reactions are tabulated in a previous paper, P. Harteck and R. R. Reeves, "Chemical Reactions in the Lower and Upper Atmosphere" Interscience Publishers (Wiley), 1961, p. 219

4. P. Harteck and U. Kopsch, Z. Physik Chem, B12, 327 (1931).

5. D. D. Woodbridge; "Chemical Reactions in the Lower and Upper Atmosphere" Interscience Publishers (Wiley), 1961, p. 373

6. We like to acknowledge that the experiments with metal-organic compounds were prompted by discussions with Drs. N. W. Rosenberg and D. Galumb of Air Force Cambridge Research Laboratories.